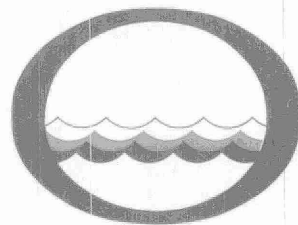


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PHOSPHORUS REMOVAL

BY

CHEMICAL ADDITION

TO AN

EXTENDED AERATION

ACTIVATED SLUDGE PLANT



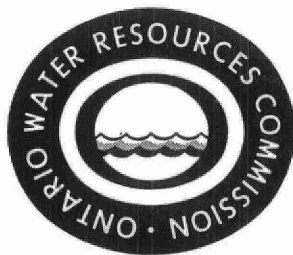
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PHOSPHORUS REMOVAL
BY
CHEMICAL ADDITION
TO AN
EXTENDED AERATION ACTIVATED SLUDGE PLANT

By
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March, 1971

Division of Research
Publication No. 39

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INTRODUCTION

It has generally been accepted that phosphorus is the nutrient most likely to be naturally limiting to algal growth in our fresh water lakes. Interest is therefore being directed towards the removal of phosphorus from municipal wastes as a major step in controlling the eutrophication of these waters.

Phosphorus is concentrated in a water body because of its rapid uptake by aquatic life and its deposition to the bottom sediments. It has been estimated in the 1969 Report to the International Joint Commission on the Pollution of Lake Erie, Lake Ontario and the International Section of the St. Lawrence River that of the total input of phosphorus entering Lake Erie only 16 percent leaves the lake through the outlet. Because of the vast interconnections within our waterbodies, whether small recreational reservoirs or large lakes, within the Great Lakes Watershed, all sources of phosphorus input should be reduced as much as is feasible. Phosphorus removal should therefore be considered for all sewage treatment installations regardless of their size.

The extended aeration process is a modification of the activated sludge process and was developed for use in smaller municipalities. This process generally requires and

also receives less supervision and maintenance than the more sophisticated conventional process since its long aeration period makes it less susceptible to sudden upsets.

There are many plants using this process now in operation throughout Ontario and it is still frequently proposed for small municipalities and also for institutional or service centre installations. In view of the present concern over phosphorus and its removal from sewage, the Division of Research was requested by the Division of Sanitary Engineering to carry out an investigation to determine the feasibility of chemically removing phosphorus from sewage within an extended aeration activated sludge plant.

For purposes of this study, it was decided to use an operating plant and that no extra supervision would be given to the plant process during this investigation. The plant was to be allowed to operate in its normal manner if possible.

The Kleinburg Sewage Treatment Plant (STP) was selected, with factors entering into its choice including location, design and operating capacity and plant layout. The Kleinburg STP is an extended aeration modification of the

activated sludge process and although its design capacity is 9.48 m³/h (50,000 I gpd) present flow to the plant is approximately 4.74 m³/h (20,000 gpd). The plant, however, has been designed essentially as two complete units and as only one unit is being used, that unit is operating near its design capacity.

CHEMICAL REMOVAL OF PHOSPHORUS

Chemical treatment of sewage for phosphorus removal at an activated sludge plant may involve, a) the chemical treatment of raw sewage, b) the chemical treatment of activated sludge effluent, or c) combined chemical-biological treatment.

In the chemical treatment of raw sewage, chemical flocculation and precipitation occur in units prior to the aeration facilities. Such a process may suitably be adapted at a reasonable cost to those plants with primary clarifier facilities. Compounds of iron, aluminum or calcium are generally equally effective.

In the chemical treatment of activated sludge effluent, chemical flocculation and precipitation occurs in specially constructed flocculator/clarifier units. Such a process therefore necessitates the outlay of considerable capital expense. Alum or lime may be used in such processes, but iron compounds may result in the carryover of iron into the receiving water.

As the Kleinburg STP does not have primary settling facilities and since this study did not warrant a large capital expenditure the third process, the combined chemical-biological process was used.

The combined chemical-biological process involves the addition of a metal salt directly into the aeration tank of the activated sludge process resulting in the formation and precipitation of only slightly soluble phosphorus compounds. Chemicals containing aluminum or iron such as alum or ferric chloride are commonly used since they are least likely to interfere with the biological processes.

The combined chemical-biological process has been studied by many investigators on laboratory and pilot scale installations. Perhaps the most extensive study of this process was carried out by Eberhardt and Nesbitt (2) using aluminum sulfate. They concluded from their results that essentially complete soluble phosphorus removals are attainable by the combined process. Similar conclusions have been drawn by other investigators (3, 6, 7, 8). In each of these investigations, however, the period of continuous chemical addition was less than four weeks. More recent works by Popel (5) and Bebin (1) have indicated that under prolonged operation of the combined chemical-biological process, deterioration of treatment quality as measured by BOD and SS content of the effluent occurred following an increase in non-volatile solids within the system.

Trials were run for this study at the Kleinburg STP using alum and iron chloride.

Plant Description

The Kleinburg STP has influent works consisting of a comminutor followed by a raw sewage holding tank of 264 m³ (50,000 I. gal.) capacity for storm flow equalization. The plant has two identical, parallel aeration tanks with a design detention of 24 hours. Air is supplied by a coarse bubble diffuser system.

Mixed liquor separation is provided for in two separate final settling tanks each with a detention time of 4.3 hours. These tanks have been designed with a surface settling rate of 0.46 m/hr (230 gal/sq. ft./day) and a weir loading rate of 0.77 m³/hr. (1,250 gal/lin.ft/day). The final effluent passes through a chlorine contact chamber before being discharged into the Humber River.

Sludge return to the aeration tanks is provided by variable air lift pumps with a return flow capacity range from 100 to 300% of design.

A single stage digester of 38.7 m³ (1366 cu.ft.) capacity treats the waste activated sludge before land disposal.

Normal Plant Operation

As mentioned, the average sewage flow to the plant is approximately one-half of that of design and therefore, only one aeration tank and final settling tank unit are used at one time. The sewage holding tank at the head of the plant is used to store the excess flow which is then passed on through the plant during low flow periods. In this way, only very infrequently does the flow through the plant exceed $4.74 \text{ m}^3/\text{hr}$ (25,000gpd).

Under normal operation, the Kleinburg STP operates as a typical extended aeration activated sludge plant. With an influent Biological Oxygen Demand (BOD) of about 160 mg/l, an average reduction of 92% is achieved through the plant process. An 80% reduction of the 194 mg/l Suspended Solids (SS) influent is also effected. Total phosphorus, at an influent concentration of about 12 mg/l, receives a typical 25% reduction.

The condition of the aeration mixed liquor is significantly influenced by the clay content of runoff infiltration to the sewer system. Under normal operation during dry weather periods, the mixed liquor suspended solids (MLSS) content averages between 8,000 to 9,000 ppm with a volatile fraction of 40 to 50%. During periods of heavy rainfall and high clay infiltration, because there are no primary clarifiers in which to settle the clay materials, the MLSS content may reach as high as 15,000 ppm with a reduced volatile content of 25 to 30%.

Table I

Summary of Kleinburg STP Data During Normal Operation

	Raw Sewage	Final Effluent	Aeration M.L.	Digester Sludge
Total Phosphorus (mg/l as P)	12	9	220	440
% Reduction		25		-
BOD (mg/l)	160	13	--	--
% Reduction		92		-
Suspended Solids (mg/l)	194	39	8220	--
% Reduction		80		-
% Volatile SS	--	71	46	--
Total Solids (mg/l)	1061	860	8970	41,060
Kjeldahl Nitrogen (mg/l as N)	54	3.1	--	--
Nitrate Nitrogen (mg/l as N)	trace	37	--	--
Aluminum (mg/l)	3	0.8	195	7125
Iron (mg/l)	4	0.5	160	640

During the chemical addition studies the periods of heavy rainfall were too infrequent to have any pronounced effect on the MLSS content.

Waste activated sludge is pumped to the aerobic digester for digestion and partial thickening.

Table I presents average data for normal plant operation.

Alum Addition for Phosphorus Removal

Method:

Alum addition to the Kleinburg STP was carried out from August 12 to October 4, 1970 for a total period of 54 consecutive days. Dry powdered alum was fed into the influent channel of the aeration tank at a rate so as to give a 230 mg/l concentration of alum to the anticipated average raw sewage flow of 4.54 m³/hr (24,000gpd). No attempt was made to proportion the chemical feed rate directly to that of the flow.

Daily 24-hour composite samples of raw sewage and final effluent were collected, and samples were submitted for analysis of Biochemical Oxygen Demand (BOD); Chemical Oxygen Demand (COD); Total Solids (TS); Suspended Solids (SS); Volatile Suspended Solids (VSS); All Nitrogen forms; Total and Soluble Phosphorus; and, Aluminum (Al⁺⁺⁺). It should be noted that the raw sewage sampler was located between the holding tank discharge and the aeration tank inlet. Final

effluent was obtained from the final clarifier effluent trough.

Daily grab samples of aeration mixed liquor and digester sludge were taken and submitted for analysis of TS, SS, VSS, Total Phosphorus, and Aluminum. Daily on-site determinations were made of Aeration Mixed Liquor Temperature; Aeration Mixed Liquor and Digester Sludge Respiration Rate; and, 30-minute Settling of Aeration Mixed Liquor. Periodic tests were made for pH, Alkalinity, Hardness and Iron content of raw sewage, final effluent, aeration mixed liquor and digester sludge. Daily flow totals were obtained from the flow totalizer located just ahead of the aeration tank inlet.

Results:

During the course of this study, there were several periods of mechanical failure and upsets in process operation during which times the process could not possibly function in its proper manner. For example, the flow was switched from one aeration tank and final settling tank unit to the other on two occasions because of mechanical problems. To effect these changes the contents of the operating aeration tank were pumped to the holding tank to be in turn, pumped back through the newly started up unit. On another occasion the sludge return pump was inadvertently turned off for a 24-hour period. Besides these major upsets, as well as numerous minor problems, there were two occasions when the raw sewage pumps were plugged.

For purposes of this report, it was decided that all operating data would be excluded at times when poor results were obtained which could be directly attributed to the above mentioned problems. It is, however, realized that such upsets are not uncommon to the minimum supervised extended aeration processes. It should be noted that no data was rejected during the two week period from September 20 to October 4.

Table II presents a summary of much of the data collected during the alum addition period. As can be seen, no improvements were made in relation to normal operating BOD and SS removals but the average Total Phosphorus reduction was increased from 33% to 91% with an effluent Total Phosphorus average concentration of 1.5 mg/l. Using all collected data, the effluent Orthophosphate concentration averaged 0.4 mg/l for the study, and the Total Phosphorus reduction averaged 69%.

Under normal operation, the SS content of the effluent averaged 39 mg/l of which 71% was of the volatile fraction. During the alum addition, the effluent SS concentration averaged 55 mg/l of which only 46% was volatile. The bulk of the increased suspended material in the final effluent during the alum addition phase was therefore due to a carryover of chemical sludge. The effluent Al^{+++} content increased from 0.8 to 4.8 mg/l. The BOD reduction remained about the same as during normal operation.

Although the effluent SS content of an extended aeration plant is expected to be somewhat higher than that from a conventional activated sludge plant, this high level during alum addition would definitely be unacceptable under most circumstances.

Table II *

Summary of Kleinburg STP Data during Alum Addition

	Raw Sewage	Final Effluent	Aeration M.L.	Digester Sludge
Total Phosphorus	17	1.5	391	776
% reduction	91		-	
BOD	163	14	-	-
% reduction	91		-	
Suspended Solids	324	55	16,046	-
% reduction	83		-	
% Volatile SS	-	46	23	-
Total Solids	1061	1010	17,100	35,197
% Volatile T.S.	23	26	27	24
Kjeldahl Nitrogen	57	2.8	-	-
Nitrate Nitrogen	trace	31	-	-
Aluminum	21	4.8	905	1670
Iron	4	0.6	210	640
Hardness (mg/l as CaCO ₃)	352	333	-	-
Alkalinity (mg/l as CaCO ₃)	442	132	-	-

* Units of parameters are as presented in Table I

Popel (5) found that subsequent coagulation with alum (alum addition to a secondary effluent) produced a much clearer effluent than simultaneous coagulation with alum (alum addition to the aeration tank). He attributed the increased turbidity during simultaneous coagulation to the high turbulence within the aeration tanks.

The aluminum content of the raw sewage presented in Table II requires an explanation. During the alum addition study this averaged 21 mg/l with some readings reaching as high as 150 mg/l and yet there are no industries connected to the sewers which would contribute such high values. The high aluminum content of the raw sewage has therefore been attributed to the emptying of the aeration tank to the holding tank on two occasions.

No appreciable difference was noted in levels of the various nitrogen components of the final effluent with that obtained during normal operation. Typical of an extended aeration process, a high degree of nitrification is achieved.

The aeration Mixed Liquor Suspended Solids (MLSS) content of the Kleinburg STP is normally maintained at about 8,000 mg/l, with a sludge return rate of 300% of design flow. During the alum addition period a MLSS concentration of 16,000 mg/l was soon reached and maintained. The volatile portion, however decreased from 46% to 23%. Similarly the total phosphorus content of the mixed liquor increased from 220 mg/l to 390 mg/l and the Al^{+++} concentration increased from 195 mg/l to 905 mg/l after about 1 1/2 weeks of study.

A comparison of respiration rates of the aeration mixed liquor before and during alum addition indicated no appreciable effect on bacterial activity due to the alum, although there was a definite change in microorganism population. During this study, the protozoan fauna disappeared completely within the first few days of alum addition and did not reappear until some time after the completion of the subsequent iron addition study.

During the study, the total phosphorus and Al^{+++} contents of the digester sludge increased also from 440 mg/l to 776 mg/l for phosphorus and from 1125 mg/l to 1670 mg/l for aluminum.

Sludge is hauled from the digester about every 10 weeks with normally about 36.3 m^3 (8,000 gal) of sludge at a solids content of 3.6% being withdrawn. Sludge was hauled on September 23, after 6 weeks of alum addition. A total 45.4 m^3 (10,000 gallons) were hauled at a solids concentration of about 4.7%. This indicates an increase of 30 to 50% in sludge production due to the alum addition, although only a very rough estimation was possible because of the lack of adequate data and records on normal plant operation.

Iron Addition for Phosphorus Removal

Method:

Iron addition to the Kleinburg STP was carried out from October 26 to December 4, 1970 for a total period of 59 consecutive days. For this study, a commercial grade of iron chloride was used. The material was a 95+ % pure mixture of ferrous and ferric chloride in a liquid form with a total iron chloride content of approximately 37%, the ratio of Fe^{++} to Fe^{+++} ions after delivery being approximately 1:1. For feeding purposes this solution was further diluted in a ratio of 1 part solution to 5 parts water.

Iron was fed into the aeration tank influent channel initially at a rate to give a 12.5 mg/l concentration of iron to an estimated average flow of 4.16 m³/hr (22,000 Igpd). This rate was applied until November 12 at which time it was increased to give 15 mg/l in the average flow of 4.07 m³/hr (21,500 gpd).

Samples were collected and analyses made as was done for the alum study. In this case, however, iron analyses were carried out in place of the aluminum analyses.

Results:

During this study also, there were several periods of mechanical failure and process changes which greatly affected the proper operation of the plant. Again, all operational data obtained during periods of plant upsets which could not, in any way, be attributed to the iron, were disregarded for purposes of this report.

Table III presents a brief summary of much of the data collected during the two iron concentration addition periods. Again, no appreciable effects were noted in relation to normal operating BOD and SS removals. Similarly, no difference was noted in the various nitrogen components of the final effluent with that of normal operation. Phosphorus reduction, however, was increased from 33% to 86% during the 15 mg/l level addition of iron with a resultant average effluent Total Phosphorus concentration of 2.6 mg/l. The corresponding Orthophosphate concentration of the effluent was 1.3 mg/l. Using all data collected at the 15 mg/l iron addition level, the Total Phosphorus reduction averaged 80%. No data was excluded during the 12.5 mg/l level study.

During the iron addition experiment, the effluent SS content and its volatile fraction were both similar to that of normal operation. The slightly lower volatile portion (63% as compared to 71%) of the effluent during iron addition reflects the slightly increased iron content of the effluent.

At the same rate of sludge return and wasting as in the alum study, the aeration mixed liquor suspended solids level dropped to about 13,000 mg/l. When the sludge return rate was reduced to 250% on November 18, MLSS level dropped further to about 11,000 mg/l. Total phosphorus content of the mixed liquor remained at about 400 mg/l and iron content was increased from 160 mg/l to 430 mg/l. Once again, this level of iron was soon reached and remained constant throughout the remainder of the study. The volatile content of the aeration mixed liquor suspended solids levelled out at 38%.

Summary of Kleinburg STP Data During Iron Addition *

	12.5 ppm Iron				15 ppm Iron			
	Raw Sewage	Final Effluent	Aeration Mixed Liquor	Digester Contents	Raw Sewage	Final Effluent	Aeration Mixed Liquor	Digester Contents
Total Phosphorus	13	4.1	413	1090	18.5	2.6	392	1378
% Reduction	68		-	-	86		-	-
BOD	142	16	-	-	212	12	-	-
% Reduction	89		-	-	94		-	-
Suspended Solids	139	40	13,164	55,387	440	32	11,185	42,750
% Reduction	79		-	-	- 93		-	-
% Volatile SS	-	62	33	-	-	63	38	-
Total Solids	-	820	13,894	58,523	-	-	11,903	49,954
% Volatile T. S.	-	-	34	-	-	-	39	-
Kjeldahl Nitrogen	64	2	-	-	76	2	-	-
Nitrate Nitrogen	Trace	34	-	-	Trace	24	-	-
Iron	2.7	1.0	428	1400	8.4	1.8	433	1628

* Units of parameters are as presented in Table I.

Measurement of aeration mixed liquor respiration rates indicated no adverse effects of the iron on the biological activity within the aeration tank.

The total phosphorus content of the digester sludge dropped off somewhat although a higher solids content was maintained, indicating perhaps, a more compactable sludge.

On November 25, about 40.8 m³/h (9,000 gallons) of digester sludge at a solids content of about 5.3% was withdrawn for disposal. This included the sludge from 3 weeks of alum addition, 2 weeks of no chemical addition and 4 weeks of iron addition. The sludge increase due to iron addition has been estimated as being 10 - 15% over that of normal operation.

Discussion

Removal of phosphorus from sewage by metallic salts is accomplished through the direct precipitation of orthophosphate as a metallic phosphate complex, and through the adsorption of condensed phosphates onto the hydroxide and phosphate floc of the metal. An excess of metal ions is therefore essential for the formation of the stoichiometrical amount being required. Additions of excessive quantities of aluminum or iron salts may, on the other hand, result in an impairment of the precipitate settleability. (4)

The rate of reaction between orthophosphate and Al⁺⁺⁺ and Fe⁺⁺⁺ ions is extremely rapid. Recht and Ghassemi (4) determined that the reactions of the orthophosphate ion with both Al⁺⁺⁺ and Fe⁺⁺⁺ are completed in less than 1 second.

Because of this, the metals are normally added, in the combined chemical-biological process, near the outlet end of the aeration tank. (2) This allows for the maximum hydrolysis of the condensed phosphates to take place before chemical addition and thus results in a more efficient useage of the chemical.

The Kleinburg STP, being an extended aeration modification of the activated sludge process, provides about 24 hours aeration detention in a rectangular tank. It was felt that regardless of where the chemical was added to the aeration tank it would enter into almost complete mixing with the mixed liquor. The chemical was therefore, for convenience, added to the influent channel to the aeration tank.

The solubility of Fe^{+++} and Al^{+++} phosphate is considerably affected by pH, with minimum solubility occuring at pH 4 in the case of iron and at pH 5 in the case of aluminum. (5) Adjustment of the mixed liquor pH to these low levels would, undoubtedly, aarkedly effect its biological activity and no adjustment was therefore attempted.

The results of this study have shown that high levels of phosphorus removal are possible through the addition of either Aluminum or Iron ions to the aeration tank of an extended aeration activated sludge process. Although there were frequent periods of operational problems during the study, such problems were not attributed to the use of the chemicals.

In either case, the chemical addition had little effect on the BOD removal within the plant although a significant increase in effluent SS content during the alum addition was noted.

Because of the higher solids loading in the aeration tank, one would expect the final clarifier to be more prone to upsetting if the flow rate was to exceed that of design.

During the alum addition period a considerable increase in the Al^{+++} and phosphorus content of the aeration mixed liquor was noted. Concentrations of these, however, reached a maximum after about 1 1/2 weeks of study. Such high Al^{+++} concentrations appeared to have no detrimental effects on the aeration process as reflected in a steady mixed liquor respiration rate even though the volatile portion of the suspended solids dropped from 46% to 23%.

Similarly, during the iron addition period there was an increase in the iron content of the aeration mixed liquor but no problems were experienced because of it. The increased inorganic content of the aeration mixed liquor did not appear to be detrimental to the process.

Conclusions

High levels of phosphorus removal from an operating extended aeration activated sludge plant are possible through the addition of either alum or iron chloride to the raw sewage influent channel to the aeration tank. A dosage of 230 mg/l alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$) is effective in removing in excess of 90% of the total phosphorus while a dosage of 15 mg/l iron as Fe^{+++} is effective in removing in excess of 85% of the total phosphorus.

Although the sludge produced is somewhat lighter, especially in the case of alum, than ordinary biological sludge, no difficulties should be experienced in settling out the chemical-biological sludge in a well designed settling tank as long as its design hydraulic capacity is not exceeded.

Sludge production may increase by up to 50% through the addition of 230 mg/l of alum and by 10 to 15% by the addition of 15 mg/l iron as Fe^{+++} .

At an F.O.B. Toronto cost of 6.9/Kg (\$62.50/ton) for alum in 45.359 Kg (100 lb) bags, the cost of alum would amount to approximately 1.6¢ per m^3 (\$72.00/million gallons) of sewage treated. In the case of the Kleinburg STP this would amount to about \$1.80 per day to achieve a 90% reduction in phosphorus through the use of alum. A suitable chemical feeder for alum costs approximately \$1400.00 with operational costs involving the above chemical costs, chemical storage costs, increased sludge disposal costs and the regular maintenance of the feeder. If liquid alum were used a suitable feed pump could be purchased for about \$300.00.

The cost of iron will depend upon the availability of a suitable product. If a ferrous salt is used, it must be first oxidized to its ferric state before an insoluble precipitate of phosphorus will be formed. In an extended aeration process one would expect to find adequate oxygen for this but it would be a definite consideration when dealing with a high rate process or in primary treatment.

The iron chloride used in this study was available at a cost of 9¢ per Kg (4¢/lb) F.O.B. Amherstburg, Ontario although for this study it was delivered free of charge to site by the Peace River Mining and Smelting Co. Ltd. At a dosage of 15 mg/l Fe^{+++} and a site cost of about 10¢ per Kg (\$90.00/ton) this would amount to a cost of approximately 0.44¢/m^3 (\$20.00/m.g.) of sewage treated, or in the case of Kleinburg, 50¢ per day.

At a price of about 16¢ per Kg (\$150/ton) for commercially available ferric chloride this would amount to approximately 75¢/day. Capital costs would involve corrosion protected storage and feeding equipment. Additional operational costs would involve the cost of the chemical, maintenance of the feeding equipment and the handling and disposal of the increased sludge.

This study has emphasized the fact that regardless of what sewage treatment process is employed, adequate maintenance and operational supervision is essential if desired results are to be attained.

Recommendations

This study has shown that high levels of phosphorus removal from sewage are possible through the addition of alum or iron chloride to the aeration section of an extended activated sludge plant. It is therefore recommended that such chemical addition be considered for those small plants requiring phosphorus removal.

It is also recommended that further information be obtained from full-scale studies on the effects of aluminum and iron sludge on both anaerobic and aerobic digesters. Further information should also be obtained on sludge production and handling.

The iron salt used in this study was a mixture of ferric and ferrous chloride. Further work should be carried out to determine whether there would be an advantage to using pure ferric chloride. Higher levels of iron addition should be carried out to determine the practicality of using iron salt to achieve a 90 to 95% reduction in phosphorus.

Additional studies with alum should be carried out to further define the optimum point of chemical addition in order to achieve high levels of phosphorus removal without adversely affecting the SS content of the effluent.

There is no reason, however, why all this information cannot be obtained from a full-scale operating, permanent installation.

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